



## The peculiar elongational viscosity of concentrated solutions of monodisperse PMMA in oligomeric MMA

Wagner, Manfred H.; Wingstrandt, Sara L.; Alvarez, Nicolas J.; Narimissa, Esmaeil

*Published in:*  
Rheologica Acta

*Link to article, DOI:*  
[10.1007/s00397-018-1098-4](https://doi.org/10.1007/s00397-018-1098-4)

*Publication date:*  
2018

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

### *Citation (APA):*

Wagner, M. H., Wingstrandt, S. L., Alvarez, N. J., & Narimissa, E. (2018). The peculiar elongational viscosity of concentrated solutions of monodisperse PMMA in oligomeric MMA. *Rheologica Acta*, 57, 591–601. <https://doi.org/10.1007/s00397-018-1098-4>

---

### General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# The Peculiar Elongational Viscosity of Concentrated Solutions of Monodisperse PMMA in Oligomeric MMA

Manfred H. Wagner<sup>1</sup>, Sara L. Wingstrand<sup>2</sup>, Nicolas J. Alvarez<sup>3</sup>, and Esmaeil Narimissa<sup>4</sup>

<sup>1</sup>*Polymer Engineering/Polymer Physics, Berlin Institute of Technology (TU Berlin),  
Fasanenstrasse 90, 10623 Berlin, Germany*

<sup>2</sup>*Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800  
Kongens Lyngby, Denmark*

<sup>3</sup>*Department of Chemical and Biological Engineering, Drexel University, Philadelphia,  
Pennsylvania 19104, USA*

<sup>4</sup>*Department of Chemical Engineering, Guangdong Technion–Israel Institute of Technology  
(GTIIT), Shantou 515063, China, and  
Department of Chemical Engineering, Technion–Israel Institute of Technology (IIT), Technion  
City, Haifa 32 000, Israel*

## Abstract

Concentrated solutions of nearly monodisperse poly(methyl methacrylate), PMMA-270k and PMMA-86k, in oligo(methyl methacrylate), MMA o-4k and MMA o-2k, investigated by Wingstrand et al (2015) and Wingstrand (2015) do not follow the linear-viscoelastic scaling relations of monodisperse polystyrenes (PS) dissolved in oligomeric styrene [Wagner (2014a,b); Wagner et al. (2015)]. Rather, PMMA-270k shows an attractive interaction with MMA, in contrast to the interaction of PMMA-86k and MMA. This different behavior can be traced back to different tacticities of the two polymers. The attractive interaction of PMMA-270k with o-4k creates pseudo entanglements, which increase the interchain tube pressure, and therefore the solution PMMA-270k/o-4k shows, as reported by Wingstrand et al. (2015), qualitatively a similar scaling of the elongational viscosity with  $(\dot{\epsilon}\tau_R)^{-1/2}$  as observed for polystyrene melts. For the solution PMMA-270/o-2k, this effect is only seen at the highest elongation rates investigated. The elongational viscosity of PMMA-86k dissolved in oligomeric MMA is determined by the Rouse time of the melt, as in the case of polystyrene solutions.

## Introduction

Experimental data of elongational properties of polymer solutions and melts of monodisperse and polydisperse polymers obtained by the filament stretching technique [see e.g. Bhattacharjee et al. (2002) and (2003); McKinley and Sridhar (2002); Bach et al. (2003); Nielsen et al. (2006)] have challenged the predictive capabilities of the classical Doi-Edwards (DE) tube model. In elongational flow, the tube model with the so-called independent alignment assumption predicts an upper limit of the tensile stress equal to 5 times the plateau modulus  $G_N$  [Doi and Edwards (1986)]. The tube diameter and tension in the polymer chain are assumed to be constant, and the macroscopic stress is a consequence of chain orientation only, resulting in a scaling of the steady-state elongational viscosity at strain rates  $\dot{\epsilon}$  larger than the inverse reptation time according to  $\dot{\epsilon}^{-1}$ . Various reptation-based models have invoked chain stretch when the deformation rate is larger than the inverse Rouse time  $\tau_R$  of the chain [see e.g. Pearson et al. (1989); Mead et al. (1995) and (1998); Fang et al. (2000)], and these models seem to capture the essential features seen in the elongational viscosity of polymer solutions [Bhattacharjee et al. (2002)], i.e. a decrease of the elongational viscosity proportional to  $\dot{\epsilon}^{-1}$  for elongation rates less than the inverse Rouse time, and a sudden increase at larger elongation rates.

In strong contrast to polymer solutions, elongational viscosity measurements of Bach et al. (2003) on narrow molar mass distribution polystyrene melts revealed that the elongational viscosity scales approximately with  $(\dot{\epsilon}\tau_R)^{-1/2}$  in the nonlinear viscoelastic regime. To account for this behavior and relaxing the assumption of a constant tube diameter, Marrucci and Ianniruberto (2004 and 2005) introduced an interchain pressure term arising from lateral forces between polymer chain and tube wall into the DE model, which limits chain stretching. Their analysis was restricted to scalar arguments and to the steady-state viscosity. A full constitutive equation, which describes time-dependent as well as steady-state rheology of nearly monodisperse polymer melts was presented by Wagner et al. (2005), and predictions are in excellent agreement with the elongational viscosity data of Bach et al. (2003), Hassager (2004), Nielsen et al. (2006), and Rolón-Garrido et al. (2006). Later, Wagner and Rolón-Garrido (2009a,b) proposed a combination of Rouse relaxation and tube diameter relaxation in agreement with experimental evidence of elongational flow data of monodisperse linear polymer melts, and showed that the tube diameter relaxation time is equal to three times the Rouse time. This concept

was extended to bidisperse polymer systems consisting of a short and a long chain component, and demonstrated that the effective tube diameter relaxation time of the long chain component is increased in accordance with the expansion of the tube diameter due to dynamic tube dilation [Wagner (2011)].

Huang et al. (2013a,b) investigated elongational viscosities of two polystyrene melts as well as of several concentrated solutions of the same polystyrenes with polymer volume fractions  $\phi \geq 44\%$  in oligomeric styrene, and they reported that polymer solutions show much stronger strain hardening than the corresponding melts. They also speculated on a nematic interaction between the polymer and the oligomeric styrene [Huang et al. (2013b)]. In agreement with the experimental data of Huang et al., Wagner (2014a,b) presented a unifying concept of modelling the elongational viscosity of polymer melts *and* concentrated solutions. Later, Narimissa et al. (2015, 2016a-d) extended this idea to a Hierarchical Multi-mode Molecular Stress Function (HMMSF) model for polydisperse linear and long-chain branched polymer melts.

Recently, Wingstrand et al. (2015) reported elongational viscosity data of two PMMA polymers dissolved in oligomeric MMAs. Their aim was to demonstrate linear and nonlinear universality in the rheology of polymer melts and solutions by comparing the two PMMA solutions to two polystyrene melts, PS-285k and PS-100k, with supposedly the same number of entanglements and the same number of Kuhn steps per entanglement. Also, by using MMA as solvent, the flow-induced monomeric friction reduction as proposed by Ianniruberto et al. (2012) should be similar as in the melt. Wingstrand et al. (2015) came to the conclusion that the two PMMA solutions show indeed a similar elongational viscosity as the polystyrene melts. However, their analysis was based on an empirical relation for the number of entanglements per polymer chain of the PMMA solutions. Here we examine the interaction of the two PMMA polymers with the oligomeric MMA, and present quantitative modeling of the steady-state and start-up elongational viscosities of the PMMA solution data of Wingstrand et al. (2015) and Wingstrand (2015), based on the extended interchain pressure model.

## Experimental Data and Linear-Viscoelastic Characterization

The experimental data discussed are those presented by Wingstrand et al. (2015) and Wingstrand (2015) on nearly monodisperse poly(methyl methacrylate) PMMA-270k and PMMA-86k. 44% of PMMA-270k was diluted in 4k oligo(methyl methacrylate) (o-4k), and 43% was diluted in 2k oligo(methyl methacrylate) (o-2k). The solutions were denoted as PMMA-270k/o-4k and PMMA-270/o-2k, respectively. Also, 51% of PMMA-86k was diluted in o-4k, and 43% was diluted in o-2k, and the solutions were denoted as PMMA-86k/o-4k and PMMA-86k/o-2k, respectively. Details of molecular characterization and sample preparation are given by Wingstrand et al. (2015). Elongational viscosities were measured using a filament stretching rheometer capable of measuring at high temperatures. Measurements were performed at  $150^{\circ}\text{C}$ , or shifted to  $150^{\circ}\text{C}$  by standard time-temperature shifting. The elongational viscosity data of PMMA-270k and PMMA-86k diluted in o-2k (Wingstrand 2015) have not been published previously and are reported here for the first time.

From linear-viscoelastic mastercurves of  $G'$  and  $G''$ , Wingstrand et al. (2015) determined continuous Baumgärtel-Schausberger-Winter (BSW) relaxation spectra (Baumgärtel et al. 1990). The relaxation modulus  $G(t)$  is found from the spectrum  $H(\tau)$  by

$$G(t) = \int_0^{\infty} \frac{H(\tau)}{\tau} \exp(-t/\tau) d\tau \quad (1)$$

$H(\tau)$  is composed of two part, the entanglement contribution  $H_e(\tau)$  and the glassy contribution  $H_g(\tau)$ ,

$$H(\tau) = H_e(\tau) + H_g(\tau) \quad (2)$$

with

$$H_e(\tau) = n_e G_N \left( \frac{\tau}{\tau_m} \right)^{n_e} h(1 - \tau/\tau_t) \quad (3)$$

and

$$H_g(\tau) = n_g G_N \left( \frac{\tau}{\tau_c} \right)^{-n_g} h(1 - \tau/\tau_t) \quad (4)$$

$G_N$  is the plateau modulus,  $\tau_t$  the longest or “terminal” relaxation time,  $\tau_c$  the characteristic time constant of the glassy contribution, and  $h(x)$  the Heaviside step function. The values of  $n_e$  and  $n_g$  are fixed to 0.23 and 0.70, respectively, as in the case of polystyrene melts and polystyrene

diluted in oligomeric styrene (Huang et al. 2013a,b). The other characteristic material constants of the BSW spectra for the melts and solutions investigated are summarized in Table I.

The zero-shear viscosity calculated from the BSW spectrum is given by

$$\eta_0 = \int_0^{\infty} G(s) ds = n_e G_N \tau_t \left( \frac{1}{1 + n_e} + \frac{1}{1 - n_g} \left( \frac{\tau_c}{\tau_t} \right)^{n_g} \right) \cong n_e G_N \tau_t \left( \frac{1}{1 + n_e} \right) \quad (5)$$

However, due to the slight polydispersity of PMMA-276k and PMMA-86k we prefer to determine  $\eta_0$  from a parsimonious spectrum fitted to the mastercurves of  $G'$  and  $G''$ , and this value of  $\eta_0$  is reported in Table I and is used in the following.

The entanglement molar mass  $M_e$  is obtained from the plateau modulus  $G_N$  by the relation of classical rubber elasticity as

$$M_e = \frac{\rho RT}{G_N} \varphi \quad (6)$$

with density  $\rho$  at  $150^\circ\text{C}$  taken as  $\rho = 1.130 \text{ g/cm}^3$  and gas constant  $R$ .  $\varphi$  is the volume fraction of polymer in the solution with  $\varphi=1$  specifying the melt. With  $M$  being the molar mass of the polymer, the number of entanglements per chain,  $Z$ , follows then from

$$Z = \frac{M}{M_e} \quad (7)$$

The Rouse stretch relaxation time  $\tau_R$  is calculated according to [Osaki et al. (1982); Menezes and Graessley (1982); Takahashi et al. (1993); Isaki et al. (2003)],

$$\tau_R = \frac{12 M \eta_0}{\pi^2 \rho R T \varphi} \left( \frac{M_{cm}}{M \varphi} \right)^{2.4} \quad (8)$$

$M_{cm}$  indicates the critical molar mass in the melt state and was taken as  $M_{cm} = 2M_{em}$  (see e.g. Fuchs et al. 1996), with  $M_{em}$  being the entanglement molar mass of the melt. The characteristic quantities of all PMMA melts and solutions investigated are summarized in Table I.

We note that the analysis of Wingstrand et al. (2015) was based on the empirical relations

$$Z \propto \left( \frac{\tau_t}{\tau_c} \right)^{\frac{1}{3.4}} \quad (9)$$

and

$$\tau_R = \tau_c Z^2 \quad (10)$$

which in some cases led to substantially different values for  $Z$ ,  $M_e$  and  $\tau_R$  (see values in parenthesis in Table I). These relations depend sensitively on the experimental determination of  $\tau_c$ , and deviation from values derived by relations (6) to (8) are not surprising.

**Table I.** Molecular characterization and material parameters of a) PMMA-270k and its solutions in o-4k and 0-2k, and b) PMMA-86k and its solutions in 0-4k and 0-2k at 150°C. Quantities in parenthesis as reported by Wingstrand et al. (2015).

a)

	PMMA-270k	PMMA-270k/o-4k	PMMA-270k/o-2k
<i>M<sub>w</sub></i> =270 kg/mol			
<i>MWD</i> =1.09			
$\phi$	1	0.44	0.43
$G_N$ [kPa]	408	121	125
$\tau$ [s]	229000	2610	933
$\tau_c$ [s]	0.802	0.235	0.0397
$\eta_0$ [MPa·s]	21789	56.1	23.9
$M_e$ [kg/mol]	9.7 (5.2)	14.5 (13.5)	13.7 (10.8)
$Z$ [-]	27.2 (52)	18.7 (20)	19.8 (25)
$\tau_R$ [s]	3277 (2169)	137.5 (94.0)	63.5 (24.8)
$T_g$ [°C]	141.8	120.7	108.6
$a_{T_g}$	1	0.0189	0.00340

b)

	PMMA-86k	PMMA-86k/o-4k	PMMA-86k/o-2k
$M_w=86 \text{ kg/mol}$			
$MWD=1.08$			
$\phi$	<i>1</i>	<i>0.51</i>	<i>0.43</i>
$G_N$ [kPa]	<i>1070</i>	<i>181</i>	<i>135</i>
$\tau_i$ [s]	<i>537</i>	<i>29.4</i>	<i>5.52</i>
$\tau_c$ [s]	<i>0.147</i>	<i>0.0917</i>	<i>0.0162</i>
$\eta_0$ [MPa·s]	<i>109</i>	<i>1.06</i>	<i>0.143</i>
$M_e$ [kg/mol]	<i>3.1 (6.1)</i>	<i>11.2 (12.3)</i>	<i>12.7 (14.3)</i>
$Z$ [-]	<i>23.2 (14)</i>	<i>7.7 (7.0)</i>	<i>6.8 (6.0)</i>
$\tau_R$ [s]	<i>8.04 (28.8)</i>	<i>0.77 (0.97)</i>	<i>0.19 (0.59)</i>
$T_g$ [°C]	<i>122.8</i>	<i>106.9</i>	<i>90.4</i>
$a_{T_g}$	<i>1</i>	<i>0.0757</i>	<i>0.00782</i>

The horizontal shift factors  $a_T$  used to obtain mastercurves of  $G'$  and  $G''$  at the reference temperature  $T_0=150^\circ\text{C}$  [see Wingstrand et al. (2015)] are shown in Fig.1a and 2a. The shift factors of the melts are fitted by the WLF equation

$$\log_{10} a_T = \frac{-c_1^0(T - T_0)}{c_2^0 + (T - T_0)} \quad (11)$$

with  $c_1^0 = 10.08$  and  $c_2^0 = 102.38$  for PMMA-270k, and  $c_1^0 = 13.84$  and  $c_2^0 = 180.43$  for PMMA-86k. The WLF parameters  $c_1^0$  and  $c_2^0$  are in the range of WLF parameters reported by Fuchs et al. (1996), and the difference in the temperature dependence of PMMA-270k and PMMA-86k is due to a difference in the tacticity of the two melts. The glass transition temperatures  $T_g$  of the solvents (oligomeric MMA) are much lower than the glass transition temperature of the melts,



and are reported as 98.9°C for o-4k and 72.5°C for o-2k. Therefore the glass transition temperature of the solutions as indicated in Table I is shifted by a temperature difference

$$\Delta T_g = T_{gm} - T_g \quad (12)$$

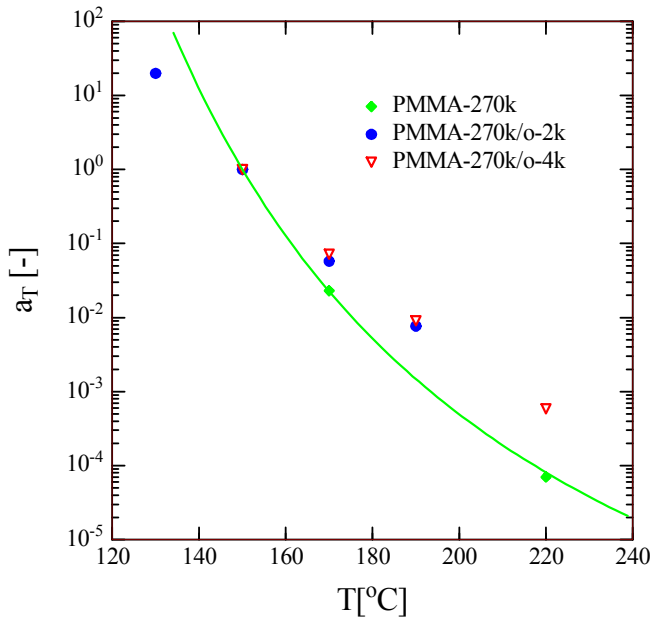
relative to the glass transition temperature  $T_{gm}$  of the melt to lower values. The change in the glass transition temperature leads to a reduction of the friction factor of the polymer solutions relative to the friction factor of the melt. Following Wagner (2014a,b), this is characterized by a shift factor  $a_{Tg}$ , which is obtained by inserting  $\Delta T_g$  from Eq.(12) into Eq.(11),

$$\log_{10} a_{Tg} = \frac{-c_1^0 \Delta T_g}{c_2^0 + \Delta T_g} \quad (13)$$

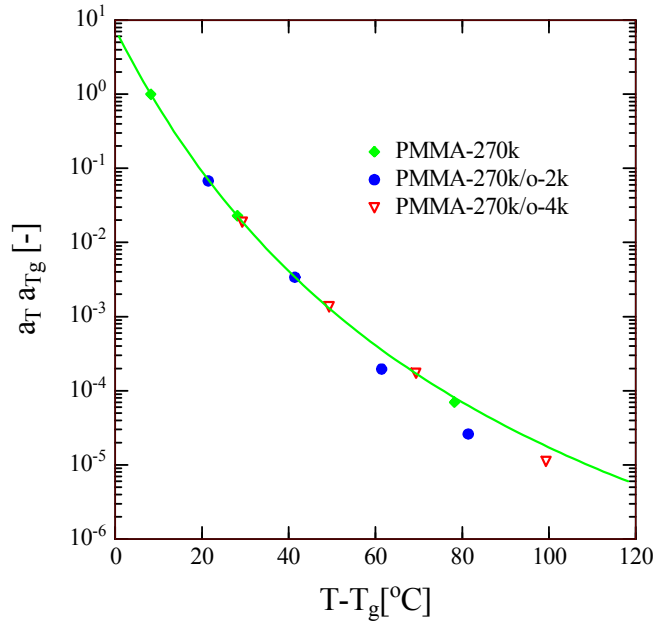
The temperature dependence of melts and solutions is then given by

$$\log_{10} a_T a_{Tg} = \frac{-c_1^0 (T + \Delta T_g - T_0)}{c_2^0 + (T + \Delta T_g - T_0)} = \frac{-c_1^0 [(T - T_g) - (T_0 - T_{gm})]}{c_2^0 [(T - T_g) - (T_0 - T_{gm})]} \quad (14)$$

The experimentally determined shift factors  $a_T$  are plotted in Fig.1b and 2b according to Eq.(14), and agreement of the temperature dependence of melts and solutions is excellent for PMMA-86k, while for PMMA-270k dissolved in MMA deviations appear at temperatures 60K (for o-2k) and 100K (for o-4k) above the glass transition temperature. A possible explanation for this is given below.



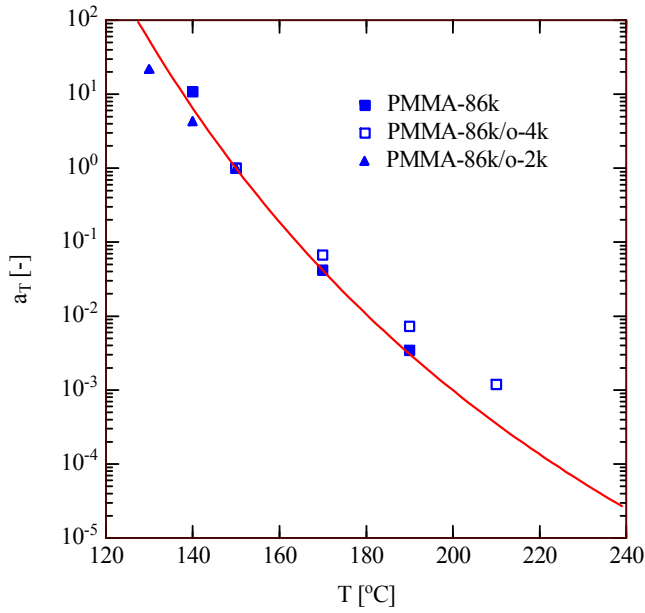
a)



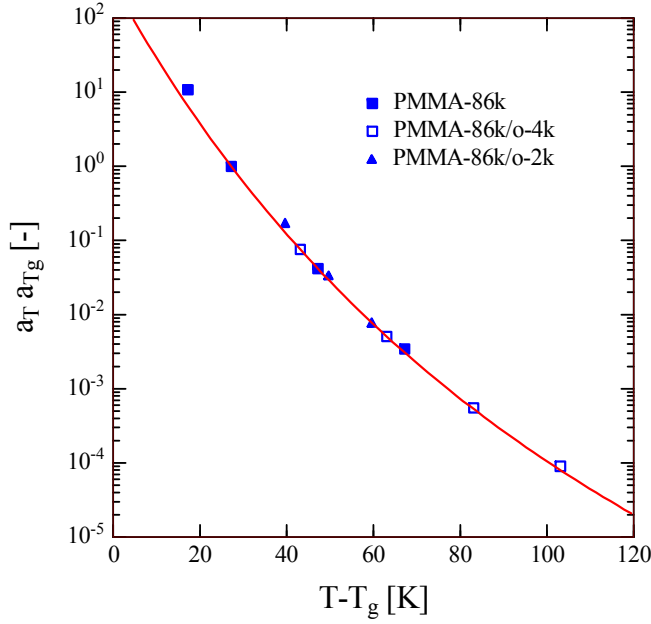
b)

**FIG.1 a)** Temperature shift factors  $a_T$  as a function of temperature for PMMA-270k melt and solutions at reference temperature of  $T_0=150^{\circ}\text{C}$  as reported by Wingstrand et al. (2015). Solid line for PMMA-270k is given by Eq.(11).

**b)** Same temperature shift factors  $a_T$  as a function of  $T - T_g$  and vertically shifted by multiplication with shift factor  $a_{T_g}$ . Solid line is given by eq.(11).



a)



b)

**FIG.2 a)** Temperature shift factors  $a_T$  as a function of temperature for PMMA-86k melt and solutions at reference temperature of  $T_0=150^\circ\text{C}$  as reported by Wingstrand et al. (2015) and Wingstrand (2015). Solid line for PMMA-270k is given by Eq.(11).

**b)** Same temperature shift factors  $a_T$  as a function of  $T-T_g$  and vertically shifted by multiplication with shift factor  $a_{T_g}$ . Solid line is given by eq.(11).

For a range of polystyrenes dissolved in oligomeric styrene with polymer volume fractions between 0.10 and 0.72, Huang et al (2013a,b) found a dilution exponent of  $\alpha=1$ , and the scaling relations with the exponents shown in Table II for polystyrene were confirmed by comparison with the experimental data [(Wagner (2014a,b); Wagner et al. (2015)]. Recently, Shahid et al. (2017) showed that the apparent dilution exponent as determined from the maximum of the loss modulus or the minimum of the loss angle scales with  $\alpha=1.3$ , and attribute this to constraint release effects. It is obvious from Table II that these scaling relations are not followed by the PMMA solutions. The entanglement molar mass  $M_e$  of both PMMA-270k/o-4k and PMMA-270k/o-2k increases with dilution much less than expected from the relation  $M_e = M_{em} \phi^{-1}$  with dilution exponents of  $\alpha=0.5$  and  $\alpha=0.4$ , respectively (Table IIa). This may be due to attractive interactions between polymer and the oligomeric solvents leading to the effective formation of pseudo entanglements between PMMA and oligomeric MMA which

enhance the elastic plateau modulus of the solutions, in spite of the fact that the molar masses of the solvents o-4k and o-2k with 3.5 and 2.1 kg/mol, respectively, are much smaller than the entanglement molar mass  $M_e=9.7\text{kg/mol}$  of PMMA-270k.

For PMMA-86k, the entanglement molar mass  $M_e$  of both PMMA-86k/o-4k and PMMA-86k/o-2k increases with dilution more than expected from the relation  $M_e = M_{em}\phi^{-1}$  (Table IIb), which may be due to a repulsive interaction between polymer and solvent., but we also note that the exponents observed are not far from the apparent dilution exponent of  $\alpha=1.3$  reported by Shahid et al. (2017). The entanglement molar mass of melt PMMA-86k resulting from Eq.(6) is  $M_{em}=3.1\text{kg/mol}$  (Table Ib), and therefore similar to the molar mass of the solvents o-4k and o-2k. By using the relation (9), Wingstrand et al. (2015) report instead an entanglement molar mass of  $M_{em}=6.1\text{kg/mol}$ . This value would result in a dilution exponent of  $\alpha\approx 1$  for both PMMA-86k/o-4k and PMMA-86k/o-2k instead of  $\alpha=1.6$  and  $\alpha=1.5$ , respectively, bringing it in line with the dilution coefficient found for polystyrene dissolved in oligomeric styrene.

Unfortunately, no information on the tacticity of the PMMA polymers and solvents investigated by Wingstrand et al. (2015) is available. However, we note that Fetters et al. (1999) report values of the plateau modulus of 310 and 760kPa for an atactic and a predominantly syndiotactic PMMA, respectively. By comparison with the data given in Table I, this indicates that PMMA-270k with  $G_N=408\text{kPa}$  is predominantly atactic, while PMMA-86k with  $G_N=1070\text{kPa}$  has a very high tacticity. Considering the difference in the temperature dependence of the shift factors of PMMA-270k and its solutions at higher temperatures as shown in Fig.1b, the attractive interaction of PMMA-270k and the oligomeric solvents seems to be temperature dependent, while the shift factors of PMMA-86k and its solutions coincide perfectly.(Fig. 2b). In summary, from the scalings presented in Table II, it is obvious that the characteristic properties of the PMMA solutions such as plateau modulus and entanglement molar mass are largely influenced by the tacticity of PMMA and its interaction with MMA.

**Table II.** Exponents “x” of scaling relations for a) polystyrene (PS) solutions and PMMA solutions in o-4k and 0-2k; and b) polystyrene (PS) solutions and PMMA solutions in 0-4k and 0-2k at 150°C.

a)

	PS solutions (Wagner 2014a,b)	PMMA-270k/o-4k	PMMA-270k/o-2k
$\phi$	0.44-0.72	0.44	0.43
$G_N = G_{Nm} \phi^x$	2	1.5	1.4
$M_e = M_{em} \phi^{-x}$	1	0.5	0.4
$\eta_0 = \eta_{0m} a_{Tg} \phi^x$	3.4	2.4	1.3
$\tau_t = \tau_{tm} a_{Tg} \phi^x$	1.4	0.6	-0.2
$\tau_c = \tau_{cm} a_{Tg} \phi^{-x}$	2	3.3	3.2

b)

	PS solutions (Wagner 2014a,b)	PMMA-86k/o-4k	PMMA-86k/o-2k
$\phi$	0.44-0.72	0.51	0.43
$G_N = G_{Nm} \phi^x$	2	2.6	2.5
$M_e = M_{em} \phi^{-x}$	1	1.6	1.5
$\eta_0 = \eta_{0m} a_{Tg} \phi^x$	3.4	3.1	2.1
$\tau_t = \tau_{tm} a_{Tg} \phi^x$	1.4	0.5	-0.3
$\tau_c = \tau_{cm} a_{Tg} \phi^{-x}$	2	3.1	3.1

### The Extended Interchain Tube Pressure Model

The tube model of Doi and Edwards (DE) (1986) assumes that the diameter  $a_0$  of the tube is constant, or equivalently the tension in the macromolecular chain remains constant and equal to its equilibrium value even for nonlinear deformations. The extra stress tensor  $\boldsymbol{\sigma}(t)$  is then a consequence of the orientation of tube segments due to the flow. The resulting constitutive equation is of the single integral form,

$$\boldsymbol{\sigma}(t) = \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} \mathbf{S}_{\text{DE}}^{\text{IA}}(t, t') dt' \quad (15)$$

if the tube segments are assumed to align independently of each other in the flow field (the "Independent Alignment (IA)" approximation).  $G(t)$  is the linear-viscoelastic shear relaxation modulus, and the relative strain measure  $\mathbf{S}_{\text{DE}}^{\text{IA}}$  is given by

$$\mathbf{S}_{\text{DE}}^{\text{IA}}(t, t') \equiv 5 \left\langle \frac{\mathbf{u}' \mathbf{u}'}{u'^2} \right\rangle_o = 5 \mathbf{S}(t, t') \quad (16)$$

$\mathbf{S}$  is the relative second order orientation tensor. The bracket denotes an average over an isotropic distribution of unit vectors  $\mathbf{u}(t')$  at time  $t'$ , and can be expressed as a surface integral over the unit sphere,

$$\langle \rangle_o \equiv \frac{1}{4\pi} \oint \sin \theta_o d\theta_o d\phi_o \quad (17)$$

At the observation time  $t$ , the unit vectors are deformed to vectors  $\mathbf{u}'$ , which are calculated from the affine deformation hypothesis (with  $\mathbf{F}^{-1}(t, t')$  as the relative deformation gradient tensor) as

$$\mathbf{u}'(t, t') = \mathbf{F}^{-1}(t, t') \cdot \mathbf{u}(t') \quad (18)$$

$u'$  indicates the length of the vector  $\mathbf{u}'$ .

The DE model does not account for any strain hardening. Doi and Edwards (1986) added a stretch process with a stretch  $\lambda$  of the tube segments to their model in order to explain the discrepancies of the DE theory at start-up of extensional flows. Pre-averaging the stretch, i.e. assuming that the stretch is uniform along the chain contour length and an explicit function  $\lambda(t)$  of the observation time, the extra stress tensor is given by

$$\boldsymbol{\sigma}(t) = \lambda^2(t) \int_{-\infty}^t \frac{\partial G(t-t')}{\partial t'} \mathbf{S}_{\text{DE}}^{\text{IA}}(t, t') dt' \quad (19)$$

Eq.( 19) required finding a stretch evolution equation, and a vast variety of concepts based on different kinetic ideas have been proposed in recent years [see e.g. Doi and Edwards(1986), Pearson et al. (1989), McLeish et al. (1998) and Mead et al. (1998)]. However, it should be noted that Eq.(19) with any function  $\lambda^2(t)$  is not in agreement with experimental results of reversed elongational flow of a monodisperse polystyrene melt [Nielsen and Rasmussen (2008)].

While in models with pre-averaged stretch, the tube diameter is always assumed to stay constant and equal to its equilibrium value  $a_o$ , stretch can also be introduced by the assumption of a strain-dependent tube diameter, as first suggested by Marrucci and de Cindio (1980). In this way, also the pre-averaging of the stretch can be avoided, which is inherently present in models based on Eq.(19) or its differential approximations. A generalized tube model with strain-dependent tube diameter was presented by Wagner and Schaeffer [(1992), (1993) and (1994)], and Wagner et al. (2001). In the Molecular Stress Function (MSF) theory, tube segment stretch  $f = f(t, t')$  is the inverse of the relative tube diameter  $a$ ,

$$f(t, t') = a_o / a(t, t') \quad (20)$$

which decreases from its equilibrium value  $a_o$  with increasing stretch. Taking into account that the tube diameter  $a$  represents the mean field of the surrounding chains, it is assumed that the tube diameter is independent of tube segment orientation. The extra stress is then given as

$$\boldsymbol{\sigma}(t) = \int_{-\infty}^t \frac{\partial G(t - t')}{\partial t'} f^2 \mathbf{S}_{DE}^{IA}(t, t') dt' \quad (21)$$

In contrast to Eq.(19), stretch in Eq.(21) does not only depend on the observation time  $t$ , but depends on the strain history: for time-dependent strain histories, chain segments with long relaxation times (i.e. at the center of the chain) experience higher stretches than chain segments with short relaxation times (i.e. at the chain ends).

Based on the so-called “interchain tube pressure” concept of Marrucci and Ianniruberto (2004), Wagner and Rolón-Garrido (2009a,b) developed an Extended Interchain Pressure (EIP) model consisting of Eq.(21) and an evolution equation for the molecular stretch  $f$ ,

$$\frac{\partial f}{\partial t} = f (\boldsymbol{\kappa} : \mathbf{S}) - \frac{1}{3} \frac{f - 1}{\tau_{Rm}} - \frac{2}{3} \frac{f^2 (f^3 - 1)}{3\tau_{Rm}} \quad (22)$$

with the initial conditions  $f_i(t, t) = 1$ . The first term on the right hand side represents an on average affine stretch rate with  $\boldsymbol{\kappa}$  the velocity gradient tensor, the second term takes into account

Rouse relaxation in the longitudinal direction of the tube, and the third term limits molecular stretch due to the interchain tube pressure in the lateral direction of a tube segment.  $\tau_{Rm}$  is the Rouse time of the melt according to Eq.(8) with  $\varphi=1$ . Excellent agreement of the EIP model with elongational viscosity data of the monodisperse melts PS390k and PS200k (Wagner and Rolón-Garrido 2009a,b) was shown, as well as excellent agreement for melt PS-285k (Wagner, 2014a,b), which is used as a comparison here and is shown in Figs.4 and 5.

In the case of the monodisperse melts PS100k and PS50k with lower molar masses, it was necessary to account for the self-dilution due to fluctuating chain ends (Wagner 2011). Introducing an effective polymer volume fraction  $w_i$  with

$$w_i = \frac{M - M_{cm}}{M} \quad (23)$$

into the evolution equation (22),

$$\frac{\partial f}{\partial t} = f (\kappa : \mathbf{S}) - \frac{1}{3} \frac{f-1}{\tau_{Rm}} - \frac{2}{3} w_i^2 \frac{f^2(f^3-1)}{3\tau_{Rm}} \quad (24)$$

resulted in improved agreement with experimental data, as shown in Fig.7 for PS100k.

For polystyrene dissolved in oligomeric styrene, due to the shift in the glass transition temperature, the Rouse time of the solutions is much smaller than the Rouse time of the melts (Wagner 2014a,b). The additional free volume created by the solvent speeds up Rouse relaxation along the tube axis, but does not affect the interchain tube pressure created by binary contacts of polymer chains. The tube diameter relaxation of the solutions is then the same as in the melt state, resulting in an evolution equation of the form

$$\frac{\partial f}{\partial t} = f (\kappa : \mathbf{S}) - \left(1 - \frac{2}{3} \frac{\tau_R}{\tau_{Rm}}\right) \frac{f-1}{\tau_R} - \frac{2}{3} \frac{f^2(f^3-1)}{3\tau_{Rm}} \quad (25)$$

Thus, even in the case of solutions, the interchain tube pressure is characterized by the Rouse time of the corresponding melt. The Rouse time  $\tau_R$  of the PS solution can be expressed in terms of the Rouse time  $\tau_{Rm}$  of the PS melt as  $\tau_R = a_{Tg} \tau_{Rm}$ , leading to an alternative formulation of the evolution equation in terms of the Rouse time  $\tau_{Rm}$  of the melt,

$$\frac{\partial f}{\partial t} = f (\kappa : \mathbf{S}) - \left(1 - \frac{2}{3} a_{Tg}\right) \frac{f-1}{a_{Tg} \tau_{Rm}} - \frac{2}{3} \frac{f^2(f^3-1)}{3\tau_{Rm}} \quad (26)$$



Evolution equation (26) was successfully used in modeling the elongational viscosity of PS dissolved in oligomeric styrene as well as in small molecule solvents (Wagner et al. 2015).

### Comparison to experimental data

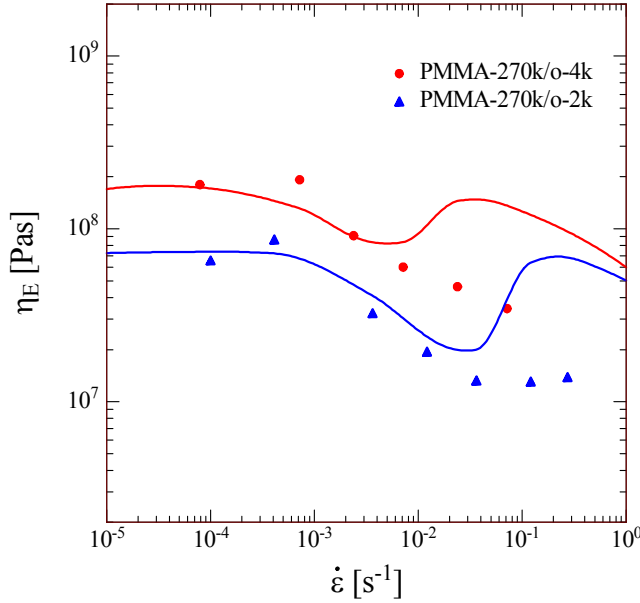
Predictions of the EIP model are now confronted with experimental evidence as presented by Wingstrand et al. (2015) and Wingstrand (2015). The parameters of the relaxation spectra for melts and solutions, Eqs.(3) and (4), are given in Table I, as well as the Rouse times calculated by Eq.(8).

#### *Solutions of PMMA-270k*

Predictions assuming that the PMMA solutions in oligomeric MMA behave in the same way as PS solutions in oligomeric styrene, i.e. using the evolution equation (26) with the Rouse time of the solution defined by  $\tau_R^* = a_{Tg} \tau_{Rm}$ , are shown in Fig.3. Predictions are in agreement with experimental evidence up to elongation rates when the Rouse relaxation term in the evolution equation diverges, i.e. for Weissenberg numbers

$$Wi_{Rm} = \dot{\epsilon} a_{Tg} \tau_{Rm} \rightarrow 1 \quad (27)$$

For PMMA-270k/o-4k and PMMA-270k/o-2k, the critical elongation rates are  $\dot{\epsilon}_c = \frac{1}{a_{Tg} \tau_{Rm}} = 0.016s^{-1}$  and  $\dot{\epsilon}_c = 0.090s^{-1}$ , respectively. At larger elongation rates, the divergence of the Rouse relaxation term is suppressed by the interchain pressure term, which, after the maximum, leads to a decreasing viscosity with a slope corresponding to  $(\dot{\epsilon} \tau_{Rm})^{-1/2}$ . The predicted behavior up to the maximum of the elongational viscosity is qualitatively similar to what is reported for PMMA dissolved in small molecule solvents [Bhattacharjee et al. 2002; Wagner et al. 2015].

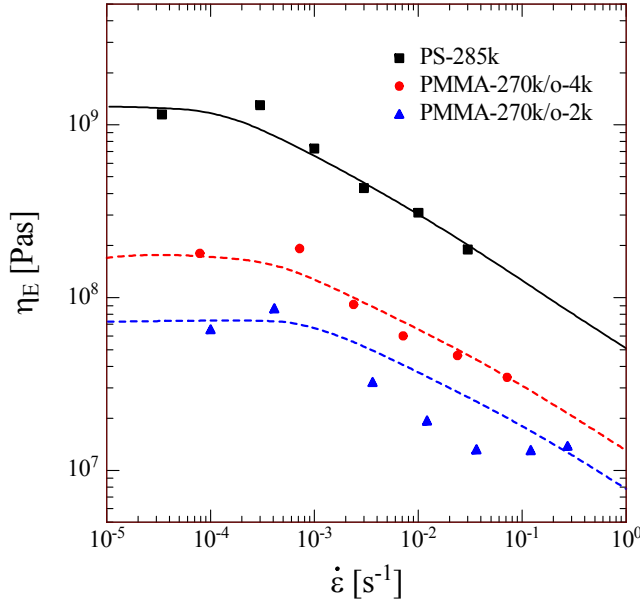


**Fig.3** Steady-state elongational viscosity data (symbols) and predictions (lines) by Eqs. (21) and (26).

On the other hand, when the PMMA solutions in oligomeric MMA are considered as melts, i.e. when the evolution equation (22) for melts is used with the Rouse times of the solutions according to eq.(8) and Table I,

$$\frac{\partial f}{\partial t} = f \left( \kappa : \mathbf{S} \right) - \frac{1}{3} \frac{f-1}{\tau_R} - \frac{2}{3} \frac{f^2(f^3-1)}{3\tau_R} \quad (28)$$

qualitative agreement between experimental evidence and predictions is obtained for PMMA-270k/o-4k, while the agreement with the data of PMMA-270k/o-2k is marginal (Fig.4). Predictions of  $\eta_E(\dot{\epsilon})$  scale with  $(\dot{\epsilon}\tau_R)^{-1/2}$  at higher strain rates, which is a signature of the interchain pressure effect. Qualitatively, as observed by Wingstrand et al. (2015), PMMA-270k/o-4k can be considered to behave as a pseudo polymer melt with the Rouse time of the solution being taken as the characteristic Rouse time of the pseudo melt, while the data of PMMA-270/o-2k show clearly a different behavior.



**Fig.4** Steady-state elongational viscosity data (symbols) and predictions (lines) by Eqs. (21) and (28).

Nearly quantitative agreement between data and model can be obtained as shown in Fig.5, when the evolution equation (26) for the solutions is used, but with the Rouse time of the melt in the interchain pressure term replaced by the Rouse time of the solution,

$$\frac{\partial f}{\partial t} = f (\kappa : \mathbf{S}) - \left( 1 - \frac{2}{3} \frac{a_{Tg} \tau_{Rm}}{\tau_R} \right) \frac{f-1}{a_{Tg} \tau_{Rm}} - \frac{2}{3} \frac{f^2 (f^3 - 1)}{3 \tau_R} \quad (29)$$

We note that in the limit of small elongation rates, eq.(29) reduces to the small stretch limit of evolution equation (26) [Wagner and Rolón-Garrido (2009a,b); Wagner (2014a,b)],

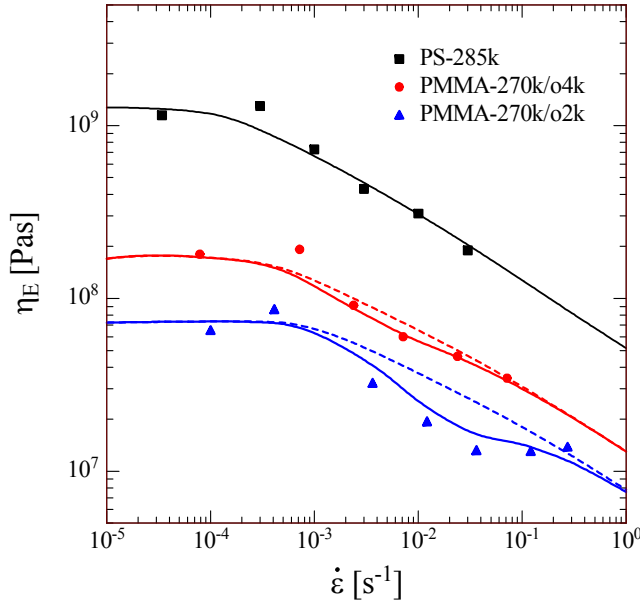
$$\frac{\partial f}{\partial t} = f (\kappa : \mathbf{S}) - \frac{1}{3} \frac{f-1}{a_{Tg} \tau_{Rm}} \quad (30)$$

while at high elongation rates, eq.(29) approaches the high stretch limit of evolution equation (28),

$$\frac{\partial f}{\partial t} = f (\kappa : \mathbf{S}) - \frac{2}{3} \frac{f^2 (f^3 - 1)}{3 \tau_R} \quad (31)$$

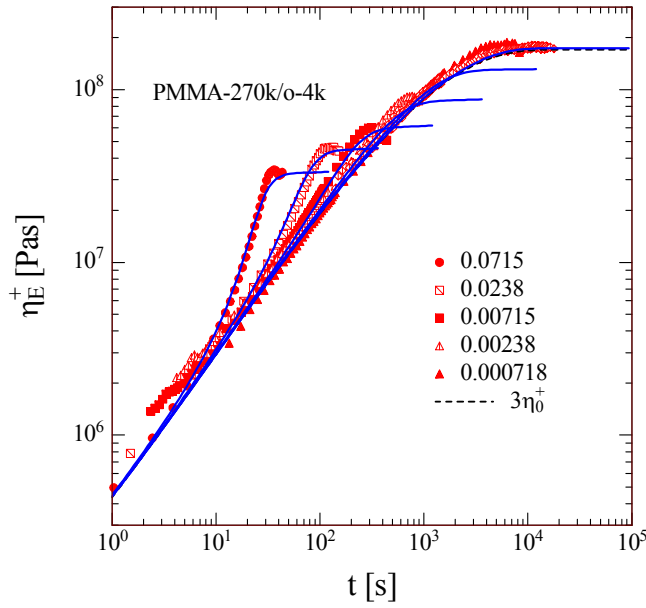
This means that Rouse relaxation in the longitudinal direction of the tube, which is effective at small elongation rates, is determined by the true Rouse relaxation time of the diluted PMMA polymer chains  $\tau_R^* = a_{Tg} \tau_{Rm}$ , unaffected by the attractive interaction with oligomeric MMA, while the interchain pressure in the perpendicular direction of the tube, which limits chain stretch

at higher elongation rates, is increased by the interaction with the oligomers and is determined by the Rouse time  $\tau_R$  of the solution as calculated from eq.(8). Note that  $\tau_R^*$  is smaller than  $\tau_R$ , with  $\tau_R^* = a_{T_g} \tau_{Rm}$  being 62.1s for PMMA-270k/o-4k and 11.1s for PMMA-270k/o-2k, respectively. Especially for PMMA-270k/o-2k, the effect of Rouse relaxation is important due to the low value of  $a_{T_g}$ , and the increase of the interchain pressure due to the presence of the MMA oligomer is only significant at the highest elongation rates investigated.

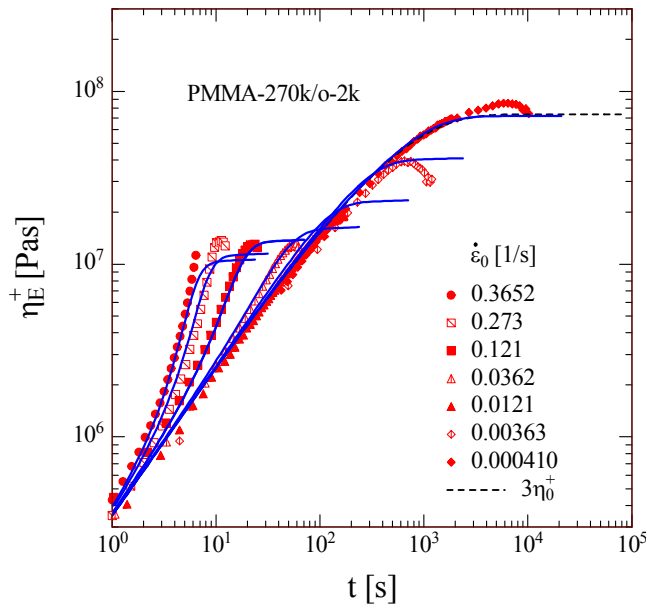


**Fig.5** Steady-state elongational viscosity data (symbols) and predictions (solid blue and red lines for PMMA solutions ) by Eqs. (21) and (29). Dotted blue and red lines for PMMA solutions and solid black line for PS are predictions by Eqs. (21) and (28).

Evolution equation (29) also gives a quantitative description of the start-up elongational viscosities of both PMMA-270k/o-4k and PMMA-270k/o-2k within experimental accuracy as demonstrated in Fig.6



a)



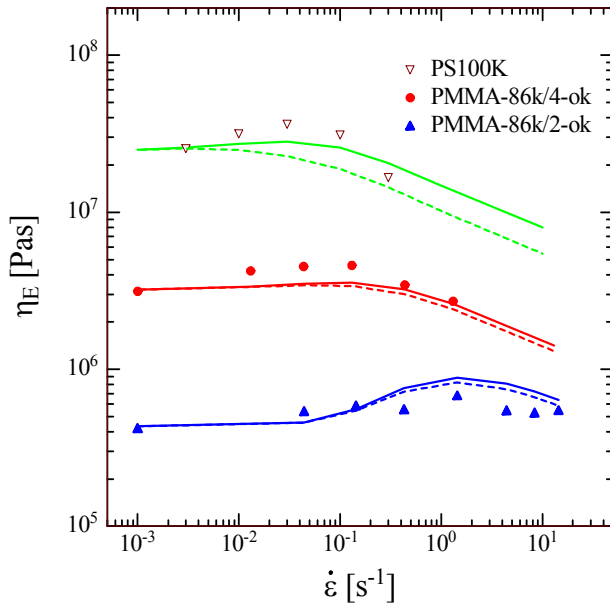
b)

**Fig.6** Start-up elongational viscosity data (symbols) and predictions (lines) by Eqs. (21) and (29).

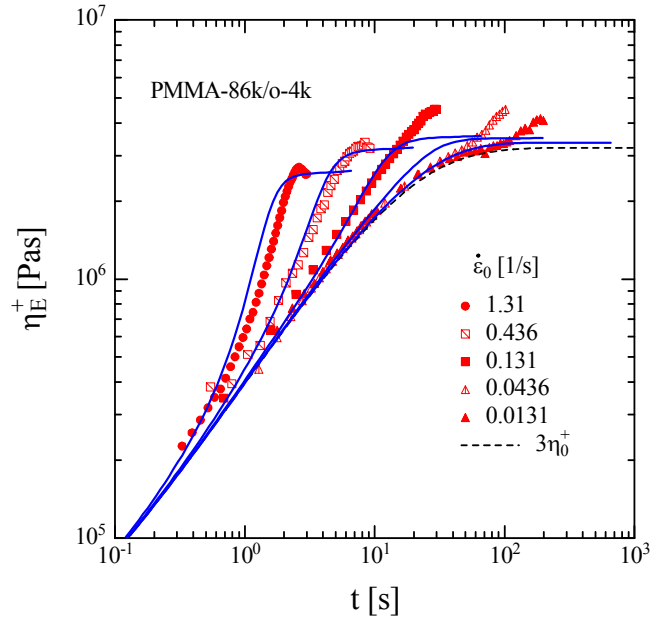
#### *Solutions of PMMA-86k*

Fig.7 shows predictions of the EIP model by use of evolution equations (22) and (24), respectively, for PS100k. Taking into account the dilution effect of the chain ends results in a

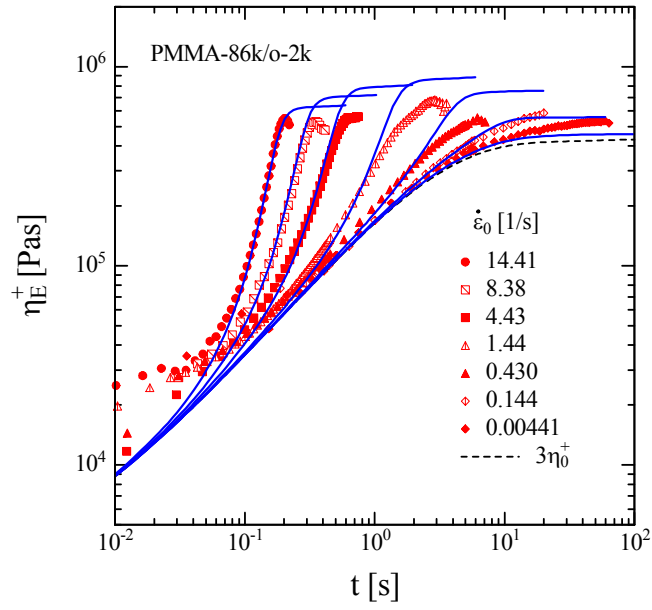
qualitative improvement of the agreement between data and model (Wagner 2011). The solutions of PMMA-86k can be considered as solutions with no attractive interaction of polymer and oligomeric solvent, and the appropriate Rouse relaxation time is, as in the case of the solutions of PS in oligomeric styrene, governed by the Rouse relaxation of the melt. Using the evolution equations (22) and (24) results in the predictions presented in Fig.7. The enhanced maximum seen in the prediction of the steady-state elongational viscosity of PMMA-86k/o-2k is caused by the terminal relaxation time  $\tau_t$  being smaller than the Rouse time  $\tau_{Rm}$  of the melt,  $\tau_t < \tau_{Rm}$ . Due to the lower value of the entanglement molar mass of PMMA-86k (Table Ib), the effect of dilution by chain end fluctuations is less pronounced than in the case of PS100k. Nevertheless, qualitative agreement between data of the steady-state (Fig.7) as well as the start-up elongational viscosity (Fig.8) and model is achieved. For a more quantitative evaluation an improved modeling of the effect of chain end fluctuations would be needed, which is outside the scope of the present paper.



**Fig.7** Steady-state elongational viscosity data (symbols) and predictions (full lines) by Eqs. (21) and (24); dotted lines predictions by Eqs.(21) and (22).



a)



b)

**Fig.8** Start-up elongational viscosity data (symbols) and predictions (lines) by Eqs. (21) and (24).



## Conclusions

The experimental data in elongational flow of two monodisperse PMMA polymers with different tacticity dissolved in two oligomeric MMAs are consistent with the assumption that the tube, i.e. the confinement of a test chain, is characterized by the orientation in the direction along the tube, and the diameter of the tube in the lateral dimension. Chain stretch is associated with a reduction of the tube diameter, and is balanced by a linear spring force in the longitudinal direction and a nonlinear interchain tube pressure in the lateral direction.

By dilution of the polymer with a solvent, the glass transition temperature  $T_g$  of the polymer in solution is reduced relative to  $T_g$  of the melt, resulting in a temperature shift factor  $a_{T_g}$ , which enters the scaling relations between melt and solutions. The PMMA solutions in oligomeric MMA investigated by Wingstrand et al (2015) and Wingstrand (2015) do not follow the scaling of polystyrene dissolved in oligomeric styrene. Rather, PMMA-270k shows an attractive interaction with MMA, in contrast to the interaction of PMMA-86k and MMA. This different behavior can be traced back to different tacticities of the two polymers. The attractive interaction of PMMA-270k with o-4k creates pseudo entanglements increasing the interchain tube pressure, and the solution PMMA-270k/o-4k shows, as observed by Wingstrand et al. (2015), qualitatively a similar scaling of the elongational viscosity with  $(\dot{\epsilon}\tau_R)^{-1/2}$  as melt PS-285k. For PMMA-270/o-2k, this effect is only observed at the highest elongation rates investigated. The elongational viscosity of PMMA-86k dissolved in oligomeric MMA is determined by the Rouse time of the melt, as in the case of polystyrene solutions. While the steady-state elongational viscosity data of PMMA-86k/o-4k show qualitatively a similar trend as PS100k with a well defined maximum followed by a decrease of the viscosity with increasing elongation rate, PMMA-86k/o-2k features a nearly constant elongational viscosity within the experimental window.

## References

- Bach, A., K. Almdal, H. K. Rasmussen and O. Hassager, "Elongational viscosity of narrow molar mass distribution polystyrene," *Macromolecules* **36**, 5174-5179 (2003).
- Baumgaertel, M, A. Schausberger, and H.H. Winter, "The relaxation of polymers with linear flexible chains of uniform length," *Rheol. Acta* **29**, 400-408 (1990).
- Bhattacharjee, P. K., J. P. Oberhauser, G. H. McKinley, L. G. Leal and T. Sridhar, "Extensional rheometry of entangled solutions," *Macromolecules* **35**, 10131-10148 (2002).
- Bhattacharjee, P. K., D. A. Nguyen, G. H. McKinley and T. Sridhar, "Extensional stress growth and stress relaxation in entangled polymer solutions," *J. Rheol.* **47**, 269-290 (2003).
- Dhole, S, Leygue, A, Bailly, C, and R. Keunings, "A single segment differential tube model with interchain tube pressure effect," *J. Non-Newtonian Fluid Mech.* **161**, 10-18 (2009).
- Doi, M., and S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford University Press, Oxford, 1986.
- Fang, J., M. Kröger and H. C. Öttinger, "A thermodynamically admissible reptation model for fast flows of entangled polymers. II. Model predictions for shear and extensional flows," *J Rheol* **44**:1293-1317 (2000).
- Fetters LJ, DJ Lohse, and WW Graessley, "Chain dimensions and entanglement spacings in dense macromolecular systems", *J. Polym. Sci. Part B: Polymer Physics* **37**, 1023-1033 (1999).
- Fox, T.G., and P.J. Flory, "Second order transition temperatures and related properties of polystyrene. I. Influence of molecular weight," *Journal of Applied Physics* **21**, 581-591 (1950).
- Fuchs, K., Chr. Friedrich, and J. Weese, "Viscoelastic Properties of Narrow-Distribution Poly(methyl methacrylates)", *Macromolecules* **29**, 5893-5901 (1996).
- Hassager, O., "Polymer fluid mechanics: Molecular orientation and stretching," *Proc. XIVth Int. Congress on Rheology*, **NF01** (2004).
- Huang Q., O. Mednova, H.K. Rasmussen, N.J. Alvarez, A.L. Skov, K. Almdal, and O. Hassager, "Concentrated Polymer Solutions are Different from Melts: Role of Entanglement Molecular Weight", *Macromolecules* **46**, 5026-5035 (2013a).
- Huang Q., N.J. Alvarez, Y. Matsumiya, H.K. Rasmussen, H. Watanabe, and O. Hassager

“Extensional rheology of entangled polystyrene solutions suggests importance of nematic interactions”, *ACS Macro Letters* **2**, 741-744 (2013b).

Ianniruberto, G., A. Brasiello, and G. Marrucci, “Simulations of fast shear flows of PS oligomero confirm monomeric fiction reduction in fast elongational flows of monodisperse PSmelts indicated ny rheoptical data”, *Macromolecules* **45**, 8058 (2012).

Isaki, T., M. Takahashi and O. Urakawa, “Biaxial damping function of entangled monodisperse polystyrene melts: Comparison with the Mead-Larson-Doi model,” *J. Rheol.* **47**, 1201-1210 (2003).

Luap, C., C. Müller, T. Schweizer, D.C. Venerus, “Simultaneous stress and birefringence measurements during uniaxial elongation of polystyrene melts with narrow molecular weight distribution,” *Rheol. Acta* **45**, 83–91 (2005).

Ferry, J.D. *Viscoelastic Properties of Polymers*; Wiley, New York, 1980.

Marrucci, G., and G. Ianniruberto, “Interchain pressure effect in extensional flows of entangled polymer melts,” *Macromolecules* **37**, 3934-3942 (2004).

Marrucci G, and G. Ianniruberto, “Modelling nonlinear polymer rheology is still challenging.” *Korea-Australia Rheol. J.* **17**(3) 111-116 (2005).

McKinley, G. and T. Sridhar, “Filament-stretching rheometry of complex fluids,” *Ann. Rev. Fluid Mech.* **34**, 375-415 (2002).

Mead, D. W., D. Yavich and L. G. Leal, “The reptation model with segmental stretch II. Steady state properties,” *Rheol. Acta* **34**, 360-383 (1995).

Mead, D. W., R. G. Larson and M. Doi, “A molecular theory for fast flows of entangled polymers,” *Macromolecules* **31**, 7895-7914 (1998).

Narimissa, E., Rolón-Garrido, V. H., and Wagner, M. H., “A Hierarchical Multi-Mode MSF Model for Long-Chain Branched Polymer Melts Part I: Elongational Flow,” *Rheologica Acta* **54**, 779-791 (2015).

Narimissa, E., Rolón-Garrido, V. H., and Wagner, M. H., “A hierarchical multi-mode MSF model for long-chain branched polymer melts part II: multiaxial extensional flows,” *Rheologica Acta* **55**, 327-333 (2016a).

Narimissa, E., and Wagner, M. H., “A Hierarchical Multi-Mode Molecular Stress Function Model for Linear Polymer Melts in Extensional Flows,” *Journal of Rheology* **60**, 625-636 (2016b).

Narimissa, E., and Wagner, M. H., “From Linear Viscoelasticity to Elongational Flow of Polydisperse Polymer Melts: the Hierarchical Multi-mode Molecular Stress Function Model,” *Polymer* **104**, 204–214 (2016c).

- Narimissa, E., and Wagner, M. H., “A Hierarchical Multi-Mode MSF Model for Long-Chain Branched Polymer Melts Part III: Shear Flow,” *Rheologica Acta* **55**, 633–639 (2016d).
- Nielsen J.K., H.K. Rasmussen, and O. Hassager, “Stress relaxation of narrow molar mass distribution polystyrene following uniaxial extension,” *J. Rheol.* **52**, 885-899 (2008).
- Nielsen J.K., and H.K. Rasmussen, “Reversed extension flow,” *J. Non-Newtonian Fluid Mech.* **155**, 15-19 (2008).
- Osaki, K., K. Nishizawa and M. Kurata, “Material time constant characterizing the nonlinear viscoelasticity of entangled polymeric systems,” *Macromolecules* **15**, 1068-1071 (1982).
- Pearson, D. S., A. Kiss, L. Fetters and M. Doi, “Flow-Induced Birefringence of Concentrated Polyisoprene Solutions,” *J. Rheol.* **33**, 517-535 (1989).
- Rasmussen, H.K., P. Laillé, and K. Yu, “Large amplitude oscillatory elongational flow,” *Rheol. Acta* **47**, 97-103 (2008).
- Rolón-Garrido V.H., M.H. Wagner, C. Luap, T. Schweizer, “Modeling Non-Gaussian Extensibility Effects in Elongation of Nearly Monodisperse Polystyrene Melts,” *J. Rheol.* **50**, 327-340 (2006).
- Shahid, T., Q. Huang, F. Oosterlinck, C. Clasena and E. van Ruymbeke, “Dynamic dilution exponent in monodisperse entangled polymer solutions”, *Soft Matter* **13**, 269-282 (2017).
- Takahashi, M., T. Isaki, T. Takigawa and T. Masuda, “Measurement of biaxial and uniaxial extensional flow behavior of polymer melts at constant strain rates,” *J. Rheol.* **37**, 827-846 (1993).
- Wagner, M. H., and J. Schaeffer, “Nonlinear strain measures for general biaxial extension of polymer melts,” *J. Rheol.* **36**, 1-26 (1992).
- Wagner, M. H., and J. Schaeffer, “Rubbers and Polymer melts: Universal aspects of non-linear stress-strain relations,” *J. Rheol.* **37**, 643-661 (1993).
- Wagner, M. H., and J. Schaeffer, “Assessment of non-linear strain measures for extensional and shearing flows of polymer melts,” *Rheol. Acta.* **33**, 506-516 (1994).
- Wagner, MH, P Rubio and H Bastian, “The molecular stress function model for polydisperse and polymer melts with dissipative convective constraint release,” *J. Rheol.* **45**, 1387-1412 (2001).
- Wagner, M.H., S. Kheirandish, and O. Hassager, “Quantitative prediction of transient

and steady-state elongational viscosity of nearly monodisperse polystyrene melts”, J. Rheol. **49**, 1317-1327 (2005).

Wagner, M.H., V.H. Rolón-Garrido, J.K. Nielsen, H.K. Rasmussen, and O. Hassager, “A constitutive analysis of transient and steady-state elongational viscosities of bidisperse polystyrene blends”, J. Rheol. **52**, 67-86 (2008).

Wagner MH, and Rolón-Garrido VH, “Recent advances in constitutive modeling of polymer melts,” *Novel Trends in Rheology III* (AIP Conference Proceedings 1152, ed. M. Zatloukal, American Institute of Physics), p.16-31 (2009a).

Wagner MH, and Rolón-Garrido VH, “Nonlinear rheology of linear polymer melts: Modeling chain stretch by interchain tube pressure and Rouse time”, Korea-Australia Rheology Journal **21**, 203-211 (2009b).

Wagner MH, “The effect of dynamic tube dilation on chain stretch in nonlinear polymer melt rheology “, J. Non-Newtonian Fluid Mech. **166**, 915-194 (2011).

Wagner MH, “Scaling relations for elongational flow of polystyrene melts and concentrated solutions of polystyrene in oligomeric styrene”, Rheol. Acta **53**, 765-777 (2014a).

Wagner MH, “An extended interchain tube pressure model for elongational flow of polystyrene melts and concentrated solutions”, J Non-Newtonian Fluid Mech. **222**, 121–131 (2014b).

Wagner, MH, E Narimissa, and VH Rolón-Garrido, “From melt to solution: Scaling relations for concentrated polystyrene solutions”, J. Rheol. **59**, 1113-1130 (2015).

Wingstrand SL, NJ Alvarez, Q Huang, and O Hassager, “Linear and Nonlinear Universality in the Rheology of Polymer Melts and Solutions”, PRL **115**, 078302 (2015).

Wingstrand SL, private communication (2015).